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This research focused on a nanoscale modification of traditional polymeric matrix morphology through particle introduction and subsequent void formation. The main areas of research have been a study of interlayer modification and analyses of continued carbon fiber reinforced polymeric matrix composites at the nanoscale. The results showed improvements in toughness up to a critical threshold, after which, an increase in the concentration and size of nanoparticulate matter and corresponding foams in the matrix deteriorated the fracture toughness properties significantly. Furthermore, nanoscale particles and foams could be used to alter the response of composite materials to a hydrothermal environment. Collectively, we are now establishing, in a reproducible manner, the placement of nanoparticles and foams in interlayer regions.

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POLYMERIC AND COMPOSITE SYSTEMS

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Executive Summary:

The research focused on the nano-modification of traditional polymeric matrix systems based on the polyanomer concept, as well as prepreg double pass impregnation processes. In addition, during this term we succeeded in running two facilities, which are in Delaware and, our new facility, in Seattle, Washington.

Status of Effort:

The application of polyanomer concepts to traditional continuous fiber reinforced composites has seen only limited research thus far. In particular, the interlaminar fracture response of these materials shows considerable promise for utilization. Both nanoscale particulates and nanoscale voids have been introduced into the matrix of traditional fiber reinforced composites to determine their influence on fracture behavior. Recent work however, even in unrelated areas, provided support to our polyanomer concept.

The need for lighter, stronger and load-bearing materials has lead to the widespread implementation of polymeric composite materials. Composite materials often exhibit synergistic properties combining the benefits of a strong and stiff reinforcing phase, with a protective matrix phase. As more traditional composite materials reach maturity, researchers have sought ways to further enhance material properties, one type that is easily processable is durable matrix. One approach that has gained considerable interest is the incorporation of a nanoscale particulate phase into a polymeric matrix. Initially, this methodology was applied to neat thermoplastic resin systems. It was soon adapted for thermosetting matrices, and more recently has seen applications as a secondary reinforcement in fiber reinforced polymer composites.

A number of different nanoscale reinforcements have been investigated. These include carbon nanotubes, vapor grown nanofibers, nanoparticulate metal oxides, and layered silicates. The layered silicates have been a particularly interesting class, owing to their low cost and broad customizability. Layered silicates have a unique platelet geometry with lengths and widths of a couple hundred nanometers, but thicknesses of only about 1 to 2 nanometers. The customizability of layered silicates is primarily attributed to the strong charge present in the gallery region between platelet layers. Although naturally containing sodium, the inter-gallery can be ion exchanged with a large number of long chain salts with various polymer compatibilities.

When properly functionalized, the silicate layers may disperse in a number of different arrangements. For comparison, the morphologies are characterized as follows: a tactoidal morphology exists when there is a lack of compatibility between particles and the matrix. The particles remain there, as received platelet spacing, and typically exhibit traditional microscale filler properties. If polymer compatibility is improved, it is possible for the polymer chains to enter the clay gallery region. As a result of this

interaction, a swelling of the clay is observed and the specimen is considered to have an intercalated nanomorphology. Under conditions of good compatibility and sufficiently high shear force mixing, it is possible for the individual platelet layers to separate and form a random exfoliated morphology.

Property enhancement tends to rely heavily on platelet morphology. Most properties are optimized with heavily randomized exfoliated morphologies. Some of the specific properties that have been improved by exfoliated morphologies are strength, stiffness, elongation to failure, gas and liquid barrier resistance, flammability and temperature resistance. The benefits of intercalated morphologies have generally been more limited, but in certain instances, they have been quite impressive. When constrained within the narrow gallery region, the polymer chains have considerably restricted mobility. Interesting responses owing to the electrical properties of these confined molecules have been reported. Another property that seems to benefit from intercalated morphology is polymer fracture toughness. It was demonstrated by Lesser et al. that when organically modified montmorillonite, a common layered silicate, was incorporated into a neat epoxy resin, the resultant material showed nearly a 100% improvement in fracture toughness. Other recent work by Karaki and Seferis, investigated the applicability of this concept to fiber reinforced composites. With specifically functionalized clays, an improvement in the fracture toughness of up to 50% was observed. Enhancement reached a maximum at 5 phr, then dropped off rapidly at 8 phr. The results suggested some enhancement in the exfoliated regime, with the effects further improved with an intercalated morphology. The drop in the fracture toughness was attributed to the tactoidal morphology and is more consistent with traditional filler results.

One limitation of the current data is the relationship among the clay modifier composition, the clay concentration, and the clay morphology. Many of the organic modifiers used to formulate the clays, act as plasticizers within the polymer matrix. Furthermore, the degree of plasticization will vary with specific modifier type. When increasing the clay concentration, an increase in the plasticizer concentration follows. In order to isolate the chemical and morphological effects in enhancing the fracture toughness, we have sought to develop processing techniques capable of producing different morphologies within the same material system.

In this supported research, we screened a number of different organically modified montmorillonite clays to determine how mixing time affects their morphology. Two of the clays, which showed a strong response to mixing time, were incorporated into the epoxy matrix of a composite prepreg. The clays were incorporated at multiple mixing times and concentrations. The fracture toughness of the cured composite specimens was characterized and the results discussed.

Accomplishments/New Findings:

We succeeded to have both microscale void and nanoscale foam epoxy matrix. The SEM photomicrographs showed the effects of the curing pressure and the styrene oxide concentration on the foam morphology. However, there were no significant effects of the

blowing agent and surfactant on the foam morphology.

Foam Density Density of the traditional epoxy matrix (control sample) was 0.0015g/mm^3 , while the density of the foam sample was 0.0014g/mm^3 and the density of the void sample was 0.0013g/mm^3 .

Mechanical Property of Epoxy Foam Matrix There was no significant difference between the 3-point bending results of the control sample and the foam sample. However, when the control sample is compared with the foam by weight, the foam was lighter than the control sample.

The results of the GIc test. There was no difference in the Mode I fracture toughness of the control sample or the void sample. This was due to the fact that crack propagation was inhibited by the presence of the foams. The existence of the foam however, was expected to affect the mechanical properties of the laminates.

The GIIC (Mode II Fracture Toughness) of the control sample, void, and foam sample. The void and foam samples had similar fracture toughness characteristics. Moreover, the fracture toughness of the control sample was higher than the void and foam samples. The foam had a deteriorating effect on the Mode II fracture toughness of the void and foam samples, although the difference of the foam morphologies of these samples was not enough to make any conclusion on the GIIC results.

Nanoscale Morphology for nanoreinforcement From our XRD results, the different clays exhibit a broad range of surface hydrophobicities, which tend to heavily influence the polymer interaction. The primary information discernible from the diffractograms is a change in average clay platelet spacing, as well as a change in the overall system order. An increase in platelet spacing from polymer intercalation is indicated by a shifting of the crystalline peak to a lower 2θ value. A reduction in peak intensity, sharpness, and area is indicative of less overall system order, but the information is somewhat limited due to interacting effects from sample preparation and X-ray transmission. D-spacing values were obtained from the manufacturer's website, though Relevant XRD data was not obtained for the natural montmorillonite clay due to the absence of crystalline peaks. In general, shifting of the crystalline peak from an as-received condition to a cured nanocomposite, showed decreasing response with increasing clay surface hydrophobicity. Within 15 minutes of mixing, Cloisite 30B exhibited, by far, the most significant shift in platelet spacing from 18.5\AA to nearly 37\AA . By comparison, the least shifting was exhibited by Cloisite 15A, which swelled only 3.8\AA . When exposed to longer mixing, only two clays exhibited a significant response. Cloisite 20A swelled an additional 2\AA and Cloisite 30B swelled an additional 4\AA with 180 minutes of mixing compared to 15 minutes. All other clays showed less than 1\AA change in d-spacing with additional mixing time. Regarding peak intensity, the greatest decrease with additional mixing was, again, observed in Cloisite 30B with a 116% decrease in intensity. The reduction in peak size is very notable, as is the sharpness of the peak. This is evidence of a reduction in the overall system order, most likely attributed to a higher percentage of exfoliated particles. Cloisite 25A also showed a large decrease in peak intensity, but the loss was not as substantial as for 30B. Based on the X-ray diffraction data, Cloisite 30B and Cloisite 20A were chosen as model nanoreinforcement systems. These clays exhibited two well-

defined and controllable morphological patterns. Cloisite 30B showed strong evidence of an intercalated morphology, which could be driven towards exfoliation with mixing. Cloisite 20A showed a very persistent stacking behavior that was susceptible to swelling, although it did not show evidence of stack disordering.

Mechanical Property of Montmorillonite CFRP Samples Composite prepreg samples, prepared with either Cloisite 30B or 20A montmorillonite, at concentrations of 2, 5 or 8 phr, with mixing times of either 15 minutes or 180 minutes, tested the Mode II fracture toughness. Compared to Cloisite 25A, which was previously investigated, the fracture toughness changes, in both of these systems, were fairly modest.

At 2 phr montmorillonite, very little change in the fracture toughness was observed for Cloisite 30B with 15 minutes or 180 minutes of mixing. Previous work on montmorillonite percolation limits has demonstrated that morphologies tend to favor more disorder at lower concentrations. For a compatible modifier at low concentrations, the particles tend to disperse fairly easily, eliminating much of the contribution of additional mixing. The 20A modified composite, which exhibits much less particle-matrix compatibility, showed a slight increase in fracture toughness with increased mixing. Continued swelling of the platelets, as well as better overall dispersion, may have led to the increase in toughness.

An increase in the concentration to 5 phr montmorillonite, again, showed very minor changes in 30B modified toughness. The 180 minutes mixing time was slightly tougher than the 15 minutes mixing time, however, the effect is small and may be attributable to better microdispersion, nanodispersion, or random error. Cloisite 20A, by comparison, exhibited a large drop in overall performance, regardless of mixing time. Based on the XRD results, it is expected that large ordered stacks of clay exist within the composite. With limited compatibility and adhesion, these stacks may act as weaknesses and stress concentrations during crack propagation. Although the 180 minutes mixed sample was expected to show evidence of greater polymer-matrix interaction, this difference may not be perceptible in such macro scale material behavior.

Between 5 and 8 phr concentrations, only the 15 minutes mixed Cloisite 30B showed an appreciable change. The fracture toughness for the 20A specimens showed little change, suggesting the locally minimized fracture toughness had already been achieved within the current fracture mechanism. At 8 phr, we expect considerably less dispersion due to more prevalent particle-particle interactions. The mixing time comparison for Cloisite 30B suggests that at lower mixing time, the clay particles are unable to readily disperse, leading to behavior more similar to the poorly bonded Cloisite 20A specimens. The large difference with longer mixing time indicates a fundamental change in the toughening mechanism, most likely due to an ability to still achieve adequate platelet separation with sufficient mixing.

NEW DISCOVERIES, INVENTIONS, AND/OR PATENT DISCLOSURES

Professor Seferis has no patents either through the universities he was affiliated with, or personally. All his work is published in open literature and he works with companies that implement his work in products and processes.

Personnel Supported

Faculty:

Professor James C. Seferis

Professional:

Dr. Chris N. Velisaris

Postdoc fellow:

Dr. Samra S. Sangari

Graduate student:

Jason P. Killgore

Other researchers:

Kyoko Ishiguro

Takuya Karaki

Misaki Takemori

Publications:

1. Peila R., Sangari S. S., Karaky T., Seferis J. C. and Parker G. "Rheological and Morphological Properties of VARTM (Vacuum Assisted Resin Transfer Molding) Epoxy Resin/ Clay Nanocomposites," Society of Plastics Engineering (SPE) 2005 Annual Technical Conference (ANTEC), Boston, Massachusetts, May 1-5 (2005).
2. Ishiguro, K. Karaki, T. Sangari, S.S. and Seferis, J.C., "Morphological and Mechanical Properties of Epoxy Foam Reinforced Composites," Society of Plastics Engineering (SPE) 2005 annual technical conference (ANTEC), Boston, Massachusetts, May 1-5 (2005).
3. Killgore, J.P., Sangari, S. S., Jensen, T., Seferis, J. C. "Cure Optimization of Layered Silicate Polyanomers," Society of Plastics Engineering (SPE) 2005 Annual Technical Conference (ANTEC), Boston, Massachusetts, May 1-5 (2005).
4. Karaki, T., Sangari, S. S., Seferis, J. C. "Effects of particle modification on the fatigue damage progress in polyanomeric matrix composite laminates," Society of Plastics Engineering (SPE) 2005 Annual Technical Conference (ANTEC), Boston, Massachusetts, May 1-5 (2005).
5. Karaki, T., Sangari, S. S., Seferis, J. C. "Tension-tension fatigue behavior of polyanomeric matrix composites," International Conference of Composite Materials (ICCM) -15, Durban, South Africa, June 27 – July 1 (2005).
6. Killgore, J. P., Sangari, S. S., Jensen, T., Seferis, J. C. "B-Stage Control of Swelling in Layered Silicate Epoxy Polyanomers," Society for the Advancement of Material and Process Engineering (SAMPE) Fall Technical Conference 2005, Seattle, WA, October 21 – November 3rd, (2005).
7. Ishiguro, K., Sangari, S. S., Seferis, J. C. "The Influence on Mechanical Properties of Epoxy Foam Matrix Structural Differentiations," Society for the Advancement of Material and Process Engineering (SAMPE) Fall Technical Conference 2005, Seattle, WA, October 21st – November 3rd, (2005).
8. Ishiguro, K., Sangari, S.S., Seferis, J.C. "Microcrack Initiation Mechanism of CFRP Under the Thermal Cycle," Society for the Advancement of Material and Process Engineering (SAMPE) Spring Technical Conference 2006, Long Beach, CA, April 30th – May 4th, (2006).

9. Seferis, J. C. "Nano-scale Control of Interfacial and Interphase Development in Polynanomatrix Composites," the annual meeting of polymer composite matrix program review, Long Beach, CA, May 5th – May 6th, (2006).

Awards and Honors received by the PI (life-time received)

Transitions:

On June 15, 2005, Professor Seferis retired from University of Washington and assumed the position of Research Professor at the Center for Composite Materials, University of Delaware. Professor Seferis and his group members accomplished their work at both the Center for Composite Materials, University of Delaware and the facilities of GloCal Network Corporation, a Delaware legal entity with facilities in Seattle, Washington. The team succeeded at performing work in the State of Delaware and Washington concurrently. After December 1, 2006, Professor Seferis and his team will continue the research, exclusively through GloCal Network Corporation and the Polymeric Composite Laboratory, now as part of the entity and transition utilization of the technology to both military and commercial airplane applications. Professor Seferis and his team will continue their research, as well as collaboration work, with people from academia and industry from all over the world.